

A sensor of sulfuric acid specific gravity for lead-acid batteries

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Abstract

On the basis of the dependence of the electrode potential on the sulfuric acid concentration, three electrodes used as the sensors have been investigated. Since, it is hard for the potential of the $\text{PbSO}_4/\text{PbO}_2$ electrode to be stable in sulfuric acid solution, this electrode is not suitable to be a sensor. For the Pb/PbSO_4 electrode used as a sensor, the stability of its potential depends on its porous structure. The higher the porosity of the negative electrode is, the shorter the response time. The potential of the Pb/PbSO_4 electrode is proportional to the logarithm of the sulfuric acid specific gravity. Compared with other sensors, this sensor developed in present work has a shorter response time, and hence, the measurement is more accurate. In the estimation of the residual capacity in a real lead-acid battery, its error is about 4%. The disadvantage of this sensor is that it still needs renewing periodically by a short charge.

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Keywords: Lead-acid battery; Sensor; Negative electrode; Sulfuric acid specific gravity

1. Introduction

The lead-acid batteries have been widely used as automotive, stationary and traction batteries and submarine batteries, etc. One of the focus issues concerning these batteries is to estimate their state-of-charge (SOC) because their residual capacity limits the energy output of the batteries. Although, much research work has been done on monitoring the SOC of the batteries or estimating their capacity [1,2], few convenient and inexpensive sensors are applied in the practical lead-acid batteries.

The methods to determine the SOC of the batteries fall into two categories. One is to use some electrical characteristics of the battery, such as impedance and voltage drop, as an indication of SOC [3,4]. The other includes various techniques to determine the concentration of the sulfuric acid in the electrolyte [5–14]. So far, the sulfuric acid concentration is the best and reliable indication of the residual capacity of the battery, such as submarine batteries and large flood stationary batteries. Sensors of sulfuric acid specific gravity have been described in many patents [5,11–13,15].

There are many methods or sensors to measure the sulfuric acid concentration in the electrolyte of lead-acid batteries. (i) The specific gravity of the sulfuric acid is measured

by use of a float (glass hydrometer), which is cheap and convenient. This method has been widely employed in practice. But, an automatic reading is hardly possible. (ii) The sulfuric acid concentration is determined by the change of the refractive index of a light in the electrolyte [5]. The problem of this method is the high price of the sensor which is complex and needs a large space. Other optical methods on the basis of the wavefront of a light and the optical fibre are also investigated [6–9]. (iii) Many authors have developed a Pb/PbO_2 electrode or the electromotive force of two electrodes to measure the sulfuric acid concentration [10–13]. These methods are based on the dependence of the electrode potential on the sulfuric acid concentration. Since, the PbO_2 and PbSO_4 are on the substrate conductive materials, such as lead, lead alloy and titanium, etc., only a mixed potential can be obtained and the potential is not stable. If the structures of the PbSO_4 and PbO_2 layers are dense, the diffusion of the sulfuric acid becomes slow and hence, the response time prolongs. Thus, the measurement error increases. The problem of these sensors is that their response time is too long and the electrode must be renewed periodically by a short charge. There are some other reference electrodes, such as $\text{Hg}/\text{Hg}_2\text{SO}_4$, $\text{Ag}/\text{Ag}_2\text{SO}_4$ and Cd stick which are often used in the field of lead-acid batteries [16,17]. Although, their potentials are determined by the sulfuric acid concentration, they are hardly applied to the indication of SOC in practice because of their sensitivity, accuracy and/or responsibility to the sulfuric acid concentration. (iv) The electric

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conductivity of the electrolyte changes with the sulfuric acid concentration. However, it reaches a maximum value at the concentration of 30% sulfuric acid so that a single-value function of the electric conductivity can not be obtained. (v) A quartz crystal microbalance is also used to determine the density of the sulfuric acid solution according to the change of the frequency of the quartz crystal, but the stray capacitance can influence the stability of the sensor in the practical measurement of a lead-acid battery [14,15]. There are also other sensors made by the high molecular compound to measure the sulfuric acid concentration [5,18].

Since, the sulfuric acid reacts with the active mass on the plates of the lead-acid battery in its charge-discharge, the measurement of the sulfuric acid concentration is an available method to indicate the capacity of the batteries. So far, the most common means of measuring its density is still the conventional and hand-operated float-type glass hydrometer, which is often used in the large flood stationary batteries and submarine batteries. However, it can not be applied to automatic monitoring. Although, the other methods mentioned above can be used to monitor the residual capacity of the battery automatically, they are not practical in reality because of the expenses, stability, resolution and the complexity of these devices. Therefore, the sensors of the sulfuric acid concentration are open to study. In this paper, a more sensitive sensor for the sulfuric acid concentration has been developed and can serve as an indication of the SOC of the battery.

2. Experimental

Since, the potentials of the Pb/PbSO₄ and PbSO₄/PbO₂ electrodes depend on the sulfuric acid concentration on the basis of Nernst equation, they can be used as the sensors to monitor the change of the sulfuric acid concentration. There were three electrodes developed in the present work. To increase the reaction area of the electrodes, the positive plate paste was pasted on the very thin Pb–Ca grid. The pasted electrodes had a dimension of 15 mm (*W*) × 8 mm (*H*) × 0.5 mm (*T*). The positive plate paste consisted of leady oxide, fibre, carbonxymethyl cellulose (CMC), H₂SO₄ and H₂O, and was mixed by hand according to the manufacture technology of the lead-acid battery. The cured and dried electrodes were used as the positive and negative electrodes and then they were formed. So, the Pb/PbSO₄ and PbSO₄/PbO₂ electrodes were obtained. A small negative plate of the lead-acid battery was also used as a sensor to compare the influence of the expander in the formulation. The measured electrode potential was against a Hg/Hg₂SO₄/H₂SO₄ (1.285 specific gravity) reference electrode. The sulfuric acid specific gravity at 25 °C was corrected by a temperature coefficient of 0.0007/K.

During the discharge of the lead-acid cell, the sulfuric acid specific gravity was monitored by the sensor of the Pb/PbSO₄ electrode prepared above. The cell consisted of

one positive plate and two negative plates, which had the same dimension of 13 cm (*W*) × 59 cm (*H*) except their thickness. The capacity of the positive plate was about 100 A h at 20 A discharge current (0.2 C rate). The monitoring of the sulfuric acid specific gravity was carried out at 10 A discharge current. And at the same time the electrolyte of the cell was taken out and measured by a glass hydrometer per 20 A h discharge, to compare with the results measured by the sensor. In the experiments, the electrode potential was recorded by a HP 34970A Data Acquisition/Switch Unit connected to a PC computer.

3. Results and discussion

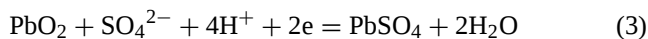
In the discharge of a lead-acid battery, the lead dioxide and lead react with the sulfuric acid in the electrolyte to form the lead sulfate on the positive and negative plates, respectively. But in the charge, the sulfuric acid gets into the solution again. The overall reaction can be expressed by



Normally, the density of the electrolyte changes in the range between 1.30 and 1.05 g cm⁻³ in the charge-discharge of various lead-acid batteries. Therefore, the sulfuric acid specific gravity can be used as an indication of the available energy that remains in the battery. And the sulfuric acid concentration can be measured by the sensor in the flood lead-acid battery.

3.1. Stability of Pb/PbSO₄ and PbSO₄/PbO₂ electrodes

Since, the reactions of the Pb/PbSO₄ and PbSO₄/PbO₂ electrodes in the charge-discharge are expressed as follows, respectively,



both potentials of positive and negative electrodes depend on the change of the sulfuric acid concentration. However, no matter which electrode is used as the sensor, it is the mixed potential that appears in the practical measurement. For the Pb/PbSO₄ electrode, the lead self-discharge occurs with the hydrogen evolution and the dissolved oxygen in the electrolyte can be reduced on it. But the negative electrode potential is mainly determined by the Pb/PbSO₄ equilibrium potential because the self-discharge rate is very low and the solubility of the oxygen is also very small. For the PbSO₄/PbO₂ electrode, there exist the reactions of the Pb/PbSO₄ and even Pb/PbO_{*n*} (1 ≤ *n* < 2) electrodes on the collector besides the PbSO₄/PbO₂ electrode. And they are thermodynamically unstable at the potential of the PbSO₄/PbO₂ electrode. Since, the lead oxidation accompanies the reduction of PbO₂, the stability of the PbSO₄/PbO₂

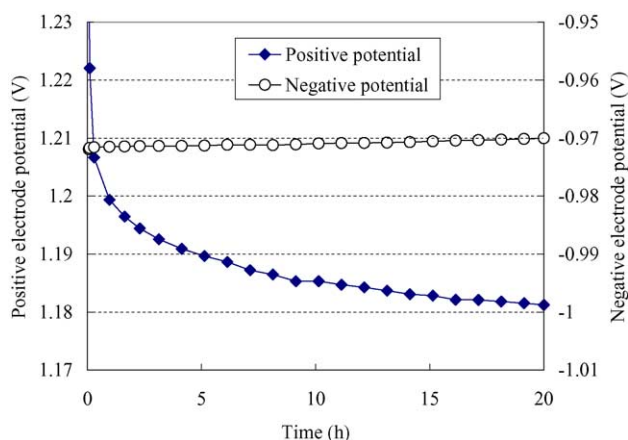


Fig. 1. The potential changes of the positive and negative electrodes as sensors in $1.285 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ at open circuit after they are overcharged.

electrode is closely related to the surface area of the lead alloy collector and its corrosion rate.

To increase the amount of the active mass and its surface area, the Pb/PbSO_4 and $\text{PbSO}_4/\text{PbO}_2$ electrodes were made by the paste on the Pb-Ca alloy grid according to the manufacture technology of the lead-acid battery. Fig. 1 shows the potential changes of the positive and negative electrodes as the sensors in the sulfuric acid solution of 1.285 g cm^{-3} after they are overcharged at 2.6 V. It is found that the potential of the negative electrode gets stable very quickly after open circuit and there is only 1.6 mV shift in the period from 6-min to 20-h. On the contrary, the positive electrode potential tends to be unstable and drops constantly. Even after an hour of open circuit, there is still a drop of 18 mV during the next 19 h. Clearly, it is attributed to the difference of the porosity between the two electrodes and the mixed potential mentioned above. During the formation, the porosity of the positive electrode decreases obviously, while that of the negative electrode increases. Consequently, it is difficult for the sulfuric acid to diffuse in the active mass of the positive electrode. In addition, the corrosion of the lead alloy is also one of the main reasons for the non-stability of the positive electrode potential. It is obvious that the positive electrode can not be used as a sensor to measure the sulfuric acid concentration of lead-acid batteries and neither can the electromotive force between the positive and negative electrodes.

Since, the response of the negative electrode is much faster than that of the positive electrode and its potential can get stable quickly, the negative electrode with a porous structure can be used as a sensor of sulfuric acid concentration. To further understand the influence of the porosity of the negative electrode on the response time and the potential stability, according to the manufacture technology of the lead-acid battery, two kinds of electrodes were prepared by the pastes of the positive and negative plates, respectively. The electrode with negative plate paste has a higher porosity because it includes the expander, which may affect the equilibrium potential of the Pb/PbSO_4 electrode. Fig. 2 shows the

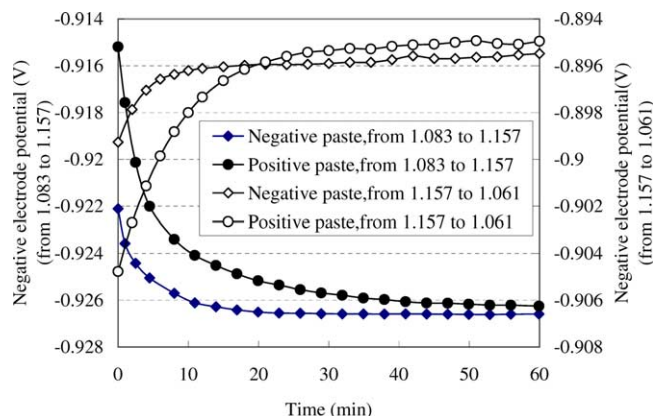


Fig. 2. The potential evolution of two negative electrodes prepared by different pastes when the density of sulfuric acid changes from 1.083 to 1.157 g cm^{-3} and then from 1.157 to 1.061 g cm^{-3} again.

potential evolution of two negative electrodes when the density of sulfuric acid changes. In the experiments, two negative electrodes always moved simultaneously from one solution to another. And the data were recorded after a few seconds. It can be seen from Fig. 2 that the potential of the negative electrode with expander becomes stable more quickly than that without expander no matter how the sulfuric acid concentration changes from dilute to dense solution or vice versa. If the electrolyte density of a lead-acid battery decreases from 1.157 ($22.2\% \text{ H}_2\text{SO}_4$) to 1.061 ($9.3\% \text{ H}_2\text{SO}_4$) g cm^{-3} , about 40% capacity will be discharged. Although, the sulfuric acid concentration changes greatly in Fig. 2, the negative electrode potential with expander gets stable after 10 min. And in the following 50 min only 0.5–0.7 mV change occurs. The negative electrode potential without expander gets stable after 20 min and there is only 0.9–1.1 mV change in the following 40 min. The potential differences between the two electrodes are 0.3 and 0.5 mV at 1 h in 1.157 and $1.061 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$, respectively. The potential of negative electrode made by the positive plate paste is slightly higher than that by the negative plate paste. This may be due to the sensitivity of the negative electrode with low porosity to oxygen dissolved in the electrolyte. Therefore, the negative electrode with higher porosity can promote the diffusion of the sulfuric acid and its sensor has a shorter response time.

3.2. Dependence of potential on density of sulfuric acid

When the Pb/PbSO_4 electrode is used as a sensor to indicate the sulfuric acid concentration, it is important to obtain its electrode potential as a function of the density of the sulfuric acid. Since, the Nernst equation of Eq. (2) can be expressed by

$$E_n = E_n^0 - \frac{RT}{2F} \ln a_{\text{SO}_4^{2-}} \quad (4)$$

the denser the sulfuric acid concentration, the higher the activity of the SO_4^{2-} ion and the more negative the nega-

tive electrode potential in Eq. (4). In the experiments, the negative electrode potential in different concentrations of the sulfuric acid was measured against the same reference electrode of $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4$ (1.285 specific gravity). So, the liquid junction potentials are different at the Luggin capillary tip of the reference electrode. Fortunately, it can be neglected because the liquid junction potentials are the same in the practical measurement and the measurement of the working curve. The evolution of the negative electrode potential were measured each time the sulfuric acid concentration changes from the dense to dilute solutions. Fig. 3 shows the very good linear relationship between the negative electrode potential and the natural logarithm of the density and according to the fitting straight line, their linear equation can be expressed by:

$$E_n = -0.3961 \ln d - 0.8702 \quad (5)$$

3.3. Measurement deviation of the sensor

When the negative electrode of the lead-acid battery is used as a sensor, the density of the sulfuric acid can be calculated by its potential in Eq. (5).

$$d = \exp\left(\frac{E_n + 0.8702}{-0.3961}\right) \quad (6)$$

The measurement deviation is given by differentiating Eq. (6).

$$\frac{dd}{dE_n} = -0.0025 \text{ g cm}^{-3} \text{ mV}^{-1} \quad (7)$$

where the negative electrode potential is against the $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4$ reference electrode. Since, the density range of sulfuric acid in the lead-acid batteries is between 1.05 and 1.30 g cm^{-3} , the measurement deviation is about 0.0026–0.0033 $\text{g cm}^{-3} \text{ mV}^{-1}$ for various sulfuric acid concentrations. It means that the measurement deviation of 1.5–2 mV will lead to about 0.005 g cm^{-3} error of sulfuric acid density. In Fig. 2, the measured potential difference

between two electrodes at 1 h is about 0.3–0.5 mV, which corresponds to the density deviation of 0.0010–0.0014 g cm^{-3} . When a lead-acid battery is discharged, the density of sulfuric acid decreases. Each change of sulfuric acid concentration in Fig. 3 means the discharge of about 20% capacity of the battery. Normally, the change of the negative electrode potential is less than 0.8 mV after 4 min in the measurement of Fig. 3. Thus, the measured density deviation is less than 0.0026 g cm^{-3} . In situ monitor and measurement by this sensor, smaller deviation will be obtained because the change of sulfuric acid concentration is slower.

3.4. In situ measurement of density for a practical lead-acid cell

The sensor consisted of the negative electrode developed above and the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode. When the lead-acid cell was discharged at 10 A, the sensor was put over the plate group and there was a space of about 1 cm in between. To reduce the IR voltage drop in the H_2SO_4 solution during discharging, the tip of the Luggin capillary was close to the surface of the negative electrode which was perpendicular rather than parallel to the positive and negative plates of the cell. In this case, the deviation or IR voltage drop in both the open circuit and discharge is only about 0.5 mV. Therefore, the density of the sulfuric acid can be obtained according to the measured potential and Eq. (6). Fig. 4 shows the change of the sulfuric acid specific gravity with the discharge of the cell. To verify the data, the electrolyte was taken out and measured by a glass hydrometer again each time 20 A h was discharged. It is found that very good linear relationship between the density of sulfuric acid and the discharge capacity occurs. After the electrolyte was measured by the glass hydrometer and returned into the cell, the sulfuric acid specific gravity increased by about 0.002 g cm^{-3} . It means that the electrolyte is uneven in the cell during its discharge and the density measured by

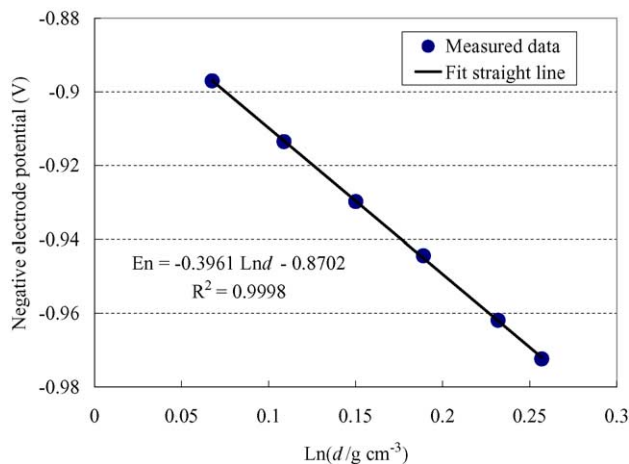


Fig. 3. The dependence of the negative electrode potential on the natural logarithm of the sulfuric acid density and their fitting straight line.

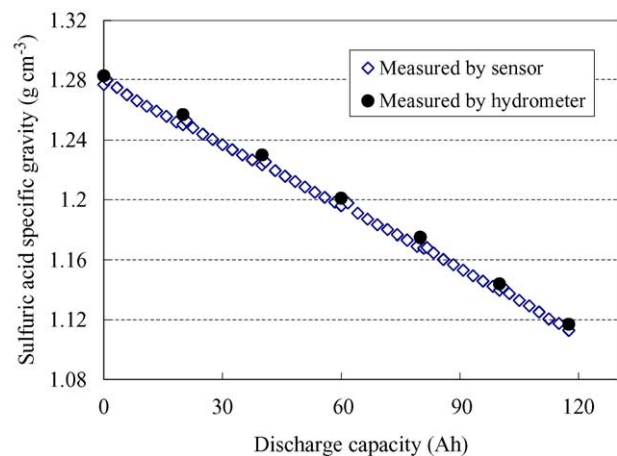


Fig. 4. The change of sulfuric acid specific gravity measured by the sensor and the glass hydrometer in the lead-acid cell at 10 A discharge current.

the sensor at this place is lower than the average electrolyte density. In in situ measurement in Fig. 4, the deviation of two methods is about 0.005 g cm^{-3} and the value obtained from the sensor is smaller. It can be calculated from the change of the density that the direct measurement error of the electrolyte density is 3% and the real capacity error, including the factors of uneven electrolyte, etc., is 4% for this cell. Therefore, the sensor developed by the negative electrode can be used as an indication of the residual capacity for the flood lead-acid batteries.

4. Conclusions

Three sensors of the sulfuric acid specific gravity have been investigated. They consist of the reference electrode and the Pb/PbSO₄ or PbSO₄/PbO₂ electrode. The potentials of latter two depend on the sulfuric acid concentration. But in fact, only the mixed potential is obtained on these electrodes. Since, the lead or lead alloy on the PbSO₄/PbO₂ electrode is thermodynamically unstable, it is difficult for its potential to be stable. So, any electromotive force, including the PbSO₄/PbO₂ electrode is not suitable to be sensors of sulfuric acid concentration. For the Pb/PbSO₄ electrode, the lead self-discharge rate with hydrogen evolution is very slow and the solubility of oxygen in the electrolyte is also very small. Consequently, the mixed potential is determined by the Pb/PbSO₄ electrode. Therefore, the Pb/PbSO₄ electrode can be used as a sensor to monitor the sulfuric acid concentration and the residual capacity of a lead-acid battery.

The response time of the sensor depends on its porous structure. The higher the porosity of the electrode, the faster the diffusion of the sulfuric acid and the shorter the response time. The Pb/PbSO₄ electrode developed in this work is of a high porosity and hence, its sensor has a high sensitivity to the change of the sulfuric acid concentration. This sensor can be used to monitor the SOC of the battery more accurately. Its working curve shows a very good linear relationship between the negative electrode potential and the natural logarithm of the sulfuric acid specific gravity. The measurement error of the electrolyte density is about $0.0026\text{--}0.0033 \text{ g cm}^{-3} \text{ mV}^{-1}$. The real error is about 4% in the estimation of the residual capacity in a lead-acid battery. Compared with other sensors composed of Pb/PbSO₄ or PbSO₄/PbO₂ electrode, this sensor has a shorter response time and hence, the measurement is more accurate. But like them, its disadvantage is that it still needs renewing periodically by a short charge.

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References

- [1] M. Hughes, R.T. Barton, S.A.G.R. Karunathilaka, N.A. Hampson, The estimation of the residual capacity of seal lead-acid cells using the impedance technique, *J. Appl. Electrochem.* 16 (1986) 555–564.
- [2] P.J. Blood, S. Sotiropoulos, An electrochemical technique for state of charge (SOC) probing of positive lead-acid battery plates, *J. Power Sources* 110 (2002) 96–106.
- [3] W.X. Shen, C.C. Chan, E.W.C. Lo, K.T. Chau, Estimation of battery available capacity under variable discharge currents, *J. Power Sources* 103 (2002) 180–187.
- [4] F. Huet, A review of impedance measurements for determination of the state-of-charge or state-of-health of secondary batteries, *J. Power Sources* 70 (1998) 59–69.
- [5] T. Yamamoto, Sulfuric acid concentration sensor and lead acid battery equipped with sulfuric acid concentration sensor, US Patent No. 5273841, 18 Dec. 1993.
- [6] C.R. Derouin, R.E. Bobbett, J.B. McCormick, W.J. Kerwin, Optical method for determining the state-of-charge of a lead-acid battery, SPIE Los Alamos Conf. Opt. Proc. SPIE 288 (1981) 349.
- [7] G.P. Hancke, A fibre-optic density sensor for monitoring the state-of-charge of a lead-acid battery, *Instrum. Meas. IEEE Trans.* 39 (1990) 247–250.
- [8] Y. Nagai, Y. Tomokuni, T. Matsui, Optical-type hydrometer for lead-acid batteries and its applications, in: *Proceedings of the INT-ELEC, International Telecommunications Energy Conference*, 1987, pp. 640–647.
- [9] T. Matsui, Portable type optical hydrometer for lead-acid batteries, *Prog. Batteries Sol. Cells* 6 (1987) 130–132.
- [10] M. Tsubota, Sensor for specific gravity of lead-acid battery electrolyte, *New Mater. New Processes* 3 (1985) 248–252.
- [11] K. Yonezu, H. Nitta, M. Tsubota, Specific gravity detecting device for lead-acid battery, US Patent No. 4689571, 25 August 1987.
- [12] P.M. Spaziant, L. Giuffrè, G. Modica, Measuring electrode for sulfuric acid concentration, US Patent No. 4262252, 14 April 1981.
- [13] J.Y. Cherng, Capacity indicator for lead-acid batteries, US Patent No. 5304433, 19 April 1994.
- [14] W. Neil, C. Garrard, J.M. Charlesworth, Application of the quartz crystal microbalance to measurement of the concentration of electrolyte in lead-acid batteries, *J. Power Sources* 56 (1995) 19–23.
- [15] T. Akutagawa, S. Sano, Sulfuric acid concentration sensor for lead storage battery, US Patent No. 5485744, 23 January 1996.
- [16] K.R. Bullock, The electromotive force of the lead-acid cell and its half-cell potentials, *J. Power Sources* 35 (1991) 197–223.
- [17] P. Ruetschi, Silver-silver sulfate reference electrodes for lead-acid batteries, *J. Power Sources* 113 (2003) 363–370.
- [18] T.B. Issa, P. Singh, M. Maker, B.S. Verma, 1,1'-Bis (11-mercapto-undecyl) ferrocene for potentiometric sensing of H⁺ ion in sulfuric acid media simulating lead acid battery electrolyte, *J. Appl. Electrochem.* 31 (2001) 921–924.

Biography

Yonglang Guo was born in 1957 in Fujian, China and received a Master's degree in 1984 and a Ph.D. in 2000, both from Department of Chemistry, Shandong University. Since 1984 he had worked in Department of Chemistry, Shandong University and in 2003 he was transferred to College of Chemistry and Chemical Engineering, Fuzhou University. His main research work is in the field of lead-acid batteries and the electrode kinetics.